EFFECT OF ADDITIVES ON ZINC – SILICON CARBIDE COMPOSITE COATING ON MILD STEEL BY ELECTRODEPOSITION

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TAREK MOKHTAR ABUBAKER ALDHIRE

Thesis submitted in fulfilment of the
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MECHANICAL AND ELECTROCHEMICAL PROPERTIES OF ZINC – SILICON CARBIDE COATED MILD STEEL DEPOSITED BY ELECTRODEPOSITION PROCESS

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LIST OF ABBREVIATIONS

AC	Alternating current
Al	Aluminum
Al_2O_3	Alumina
ASTM	American Society for Testing and Materials
C	Carbon
CNT	Carbon nanotubes
CD	Current density
CeO_2	Cerium oxide
Cr	Chromium
Cu	Copper
DC	Direct current
EDS	Energy dispersive X-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
EW_t	Equivalent weight
Fe	Iron
GPES	General purpose electrochemical system
H	Hydrogen
H_2O	Water
H_3BO_3	Boric acid
H_3PO_4	Phosphoric acid
HCl	Hydrochloric acid
HV	Vickers hardness
ICSD	Inorganic crystal structure database
Mn	Manganese

NaCl	Sodium chloride
Nb	Niobium
Ni	Nickel
O_2	Oxygen
OCP	Open circuit potential
OH^-	Hydroxide ions
P	Phosphorus
PC	Pulsed current
pH	Concentration of hydrogen ions, -log[H^+]
PRc	Pulsed reverse current
RPM	Revolutions per minute
SDS	Sodium Dodecyl Sulfate
SEM	Scanning electronic microscopy
SHE	Standard hydrogen electrode
Si	Silicon
SiC	Silicon carbide
SiO_2	Silicon oxide
TiC	Titanium carbide
TiO_2	Titanium oxide
W_{loss}	Weight loss
WC	Tungsten carbide
Wt%	Weight percentage
Wt.	Weight
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

Zn	Zinc
$Zn(OH)_2$	Zinc hydroxide
$Zn(OH)_2$	Zinc hydroxide
Zn^{2+}	Zinc ions
ZnO_2	Zinc oxide
$ZnSO_4$	Zinc sulfate
ZrO_4	Zirconium oxide

LIST OF SYMBOLS

A	Surface area of the cathode
A_W	Atomic weight
ba	Anodic Tafel coefficient
bc	Cathodic Tafel coefficient
Cc	Coating capacitance
Cdl	Double layer capacitance
CE	Current efficiency
cm	Centimeter
d	Diagonal length
d	Distance between crystal planes
d	Average grain diameter
E	Electrical field
E	Potential
e^-	Electron
E_0	Standard electrode potential
Ecorr	Corrosion potential
E_o	Amplitude of potential signal
Et	Potential at time (t)
F	Faraday constant
F	The load at fracture
f	Frequency
H	Deposit thickness
Hz	Hertz

I	Applied current
ia	Anodic current density
ic	Cathodic current density
icorr	Corrosion current density
Io	Amplitude of AC current signal
It	Current at time (t)
k	Strengthening coefficient
K	Shape factor
L	Liter
L	Crystallite size
M	Anode material
m	Meter
mA	Milliampere
mg	Milligram
mm	Millimeter
MPa	Megapascal
ms^{-1}	Millisiemens
mv	millivolt
n	Number
n	Integer
Ø	Phase angle
^{o}C	Degree celeius
P	The load applied during microhardess test
q	Charge of the particle
Q	Electric charge passed through the electrode material

Q	Constant phase element
R	Gas constant
r	Radius of particle
Rc	Coating resistance
Rct	Charge transfer resistance
Rs	Solution resistance
T	Temperature
t	Time
V	Voltage
V	Volume of deposit
V_E	Electrophoretic velocity
W	Composite coating weight per unit area
W	Mass of deposit
W1	Weight of the specimen before electrodeposition
W2	Weight of the specimen after electrodeposition
W_{Abs}	Weight of metal actually deposited
Wi	Sample weight before immersion in the corrosive solution
Wii	Sample weight after immersion in the corrosive solution
Wloss	Weight loss in the sample
W_T	Theoretical weight of deposit
Yr	Year
Z	Electrochemical equivalent
Z	Impedance
Z'	Real component of the impedance

Z''	Imaginary component of the impedance
$Z(\omega)$	The impedance at chosen frequency
Zo	Magnitude of the impedance
β	Symmetry cofficient for anodic and cathodic reaction
ω	Radial frequency
η	Viscosity of suspension
η	Over potential
η_E	Electrophoretic mobility
λ	Radiation wavelength
ρ	Density
σ	Adhesion stress
σ_0	Material constant
σ_y	Yield stress
μm	Micrometer
2θ	Diffraction angle

KESAN BAHAN TAMBAH TERHADAP SALUTAN KOMPOSIT ZINK - SILIKON KARBIDA PADA KELULI LEMBUT MELALUI ELEKTROENDAPAN

ABSTRAK

Salutan komposit Zn-SiC adalah langkah perlindungan yang berkesan untuk struktur keluli. Penambahan partikel-partikel SiC ke dalam matrik zink serta penyebaran partikel tersebut keselruhan salutan lapisan menemui masalah praktikal. Dalam usaha untuk mendapatkan salutan komposit Zn-SiC seragam dan padat menggunakan proses pengenapan elektro, parameter operasi perlu dikawal dengan baik. Pelbagai parameter operasi telah digunakan dalam kajian ini termasuklah ketumpatan arus (20, 30, 40 dan 50 mA/cm^2), kelajuan aduk (300, 400, 500, 600 dan 700 rpm) dan kepekatan SiC (5, 10, 15, 20 dan 25 g/L). Endapan zink dengan zarah SiC telah dilakukan menerusi proses elektroenapan menggunakan mandian zink sulfat mengandungi partikel SiC bersaiz 2 mikron. Parameter operasi yang terbaik diperolehi daripada kajian awal adalah ketumpatan arus 40 mA/cm^2, kelajuan aduk 600 rpm dan kepekatan SiC 20 g/L. Bagi meningkatkan pembentukan dan sifat-sifat salutan komposit Zn-SiC, elektroenapan salutan komposit Zn-SiC dengan kehadiran bahan tambahan niobium klorida dan asid fosforik pada pelbagai kepekatan telah diperkenalkan dalam kajian ini. Sifat-sifat mekanikal dan kakisan terbaik telah diperolehi dengan 10 g/L niobium klorida dan 7 g/L asid fosforik. Kadar kemasukan partikel SiC yang lebih tinggi ke dalam matriks zink telah disahkan oleh kajian SEM dan EDS. Pengurangan ketara dalam parameter kakisan salutan komposit Zn-SiC diperhatikan di mana potensi kakisan -946 mv dan -1008 mv dicapai dengan penambahan niobium klorida dan asid fosforik berbanding dengan -1100 mv yang

diperolehi bagi salutan komposit Zn-SiC tanpa bahan tambah. Mikrokekerasan salutan komposit berjaya diperbaiki dengan menggunakan bahan tambah semasa proses pengenapan. Bacaan mikrokekesaran 312 Hv dan 252 Hv diperolehi dengan 10 g/L niobium klorida dan 7 g/L asid fosforik berbadning 166 Hv bagi tanpa bahan tambah. Perubahan dalam mikrostruktur lapisan komposit Zn-SiC juga diperhatikan. Morfologi salutan, sifat mekanik dan kelakuan kakisan salutan komposit Zn-SiC mencatat peningkatan dengan kehadiran bahan tambah niobium klorida dan asid fosforik. Kehadiran bahan tambah dalam larutan mandian megakibatkam peningkatan keupayaan zeta dan mengubah caj permukaan patikel-partiekl SiC menjadi lebih positif yang menghasilkan lebih banyak partikel tertarik kepada permukaan katod. Dengai itu partikel-partikel menjadi lebih stabil disebabkan tolakan elektrostatik yang menghalang penggalomeratan dan mengakibatkan peningkatan dalam kadar kemasukan SiC dalam salutan.

EFFECT OF ADDITIVES ON ZINC – SILICON CARBIDE COMPOSITE COATING ON MILD STEEL BY ELECTRODEPOSITION

ABSTRACT

Zn-SiC composite coating is an effective protection measures for steel structures. Incorporation of SiC particles within zinc matrix as well as dispersion of these particles through the coating thickness are found a practical problem. In order to obtain uniform and dense Zn-SiC composite coating using electrodeposition process, operating parameters should be well controlled. Various operating parameters were used in this study. This includes current density (20, 30, 40 and 50 mA/cm^2), stirring speed (300, 400, 500, 600 and 700 rpm) and SiC concentration (5, 10, 15, 20 and 25 g/L). The deposition of zinc with SiC particles was performed by electrodeposition process using zinc sulfate bath containing 2 micron sized of SiC particles. The best operating parameters obtained from preliminary study were current density of 40 mA/cm^2, stirring speed of 600 rpm and SiC concentration of 20 g/L. To enhance the formation and properties of Zn-SiC composite coating, electrodeposition of Zn-SiC composite coating in presence of niobium chloride and phosphoric acid additives at various concentrations were introduced in this study. The best mechanical and corrosion properties were obtained with 10 g/L of niobium chloride and 7 g/L of phosphoric acid. The higher incorporation rate of SiC particles into zinc matrix was confirmed by SEM and EDS studies. A significant reduction in corrosion parameters of Zn-SiC composite coating was observed in which corrosion potential of -946 mv and -1008 mv were achieved with niobium chloride and phosphoric acid respectively compared with -1100 mv obtained for Zn-SiC composite coating without additives. The microhardness of the composite coating was successfully improved by using the

additives during electrodeposition process. Microhardness value of 312 Hv and 252 Hv were obtained at 10 g/L of niobium chloride and 7 g/L of phosphoric acid respectively whereas it was reached to 166 Hv without additives. The change in the microstructure of Zn-SiC composite coating to fine grains was also noted. The morphology of the coating, mechanical properties and corrosion behavior of the Zn-SiC composite coating were further improved in the presence of niobium chloride and phosphoric acid additives. The presence of additives in the bath solution led to an increase in zeta potential and change the surface charge of SiC particles to more positive which results in more particles acquired to the cathode surface. Hence, the particles were more stable in the solution due to electrostatic repulsion which preventing agglomeration of these particles and consequently increase the incorporation rate of SiC in the coating.

CHAPTER ONE

INTRODUCTION

1.1 Research Background

The deterioration of metal structures due to corrosion is one of the most serious problems in the world. Corrosion causes durability reduction for steel structures which leads to loss of billions of dollars every year. Corrosion is defined as destructive attack of a material by chemical or electrochemical reaction with its environment (Robarge, 1999). Various techniques were used to prevent corrosion damage. These include coating, cathodic and anodic protection, alternation of environment using inhibitors, design of structure (wall thickness allowance) and materials selection of metal and alloy for particular service (Sulaiman, 2014).

Coating is one of the most widely used techniques in corrosion control of the metals. The motivation for using coating on steel structures is to improve the properties of steel surface by reducing corrosion and abrasion effects in which the service life of steel structure could be extended (Fauchais et al., 2014). The coating is cost effective technique, easy to apply on metal surface and offers barrier between the metal surface and environment. These advantages make the coating preferable technique in corrosion control. The coating can be classified into organic and metallic coatings. Organic coatings are not effective enough for protecting of metals from corrosion. In fact a poor adhesion of organic coatings, under film corrosion and mechanical damage of the coating could reduce the ability of the organic coatings in protecting of metal surfaces. A satisfactory protection can be provided by metallic coatings in which barrier between metal and its environment can be formed (Uhlig and

Revie, 1985). Two types of metallic coatings namely noble and sacrificial coating are used in industry applications. Noble coatings such as copper, chrome, lead, silver and nickel are noble in galvanic series with respect to steel. A barrier layer on steel surface can be provided by noble coatings. This layer should contain minimum number of pores to prevent access of water underneath the metal coating and initiate the corrosion at steel surface. The second type of metallic coatings are sacrificial coatings. These include zinc, tin, aluminum and cadmium which are more active than steel in galvanic series and hence protect steel surface by galvanic protection.

Various process are used to deposit metallic coatings such as electrodeposition, hot dipping, flame spraying and vapor deposition process (Fontana, 1986). Electrodeposition technique is the most common technique used for applying metallic coatings on steel surface due to low cost of operation, controlling the coating thickness easily, complex structures can be deposited by this process, low energy consumption and high production rate (Tuaweri and Wilcox, 2006; Jean et al., 1999; Ullal and Hegde, 2013). One of the main purpose of electrodeposition process is to enhance the characteristics of metal surface by providing a coating that be able to resist corrosion agents and withstand the abrasion or a combination of them.

Zinc has a good corrosion resistance in all environment, this explains why used as a protective coating on variety of products. Low cost of zinc, can be used with different plating methods and easy to apply make it widely used as coating material. Most of the steel structural surfaces were protected by deposition of zinc or zinc alloy. Zinc coating can provide galvanic protection to steel substrate where potential of zinc is considerably lower than steel. In order to prevent corrosion and abrasion damage of

zinc coating, the corrosion resistance and hardness of zinc coatings should be improved.

Electrodeposition has widely used to apply zinc coating on steel sheets, particularly for automotive industries. However, the service life of electrodeposited zinc coating might be reduced due to formation of white rust corrosion on the surface of zinc coating (Hu et al., 2018). To prevent white rust corrosion, post treatment such as chromate is usually applied on zinc coating (Vathsala and Venkatesha, 2011). Due to toxic and carcinogenic nature of chromate as well as pollution problems and environmental impacts associated with using chromate process, this process was avoided and no longer in use (Sajjadnejad et al., 2015). In addition to white rust corrosion, the zinc coating on steel surface is susceptible to abrasion and mechanical damage during the service (Sajjadnejad et al., 2014a).

In order to replace chromate process and to enhance corrosion and mechanical properties of zinc coatings, the alternative technique is to deposit zinc coating with inert particles which called composite coating. In general the composite coating can be produced by the deposition of metals such as nickel, copper, chrome and zinc with ceramics and metal oxides particles. Various materials such as SiC, TiC, Al_2O_3, WC, ZrO_4 and SiO_2 are used with Ni, Cu, Zn and Cr to produce different composite coatings (Vathsala and Venkatesha, 2011). Among the ceramics, it has been reported that SiC offers good hardness and wear properties as well as improvements in corrosion behavior of metal coating (Ger, 2004; Sajjadnejada et al., 2014a). High oxidation resistance, availability and low cost of this material make SiC the best choice for producing of zinc composite coatings (Dehgahi et al., 2016).

However, the difficulties of depositing of SiC particles into zinc matrix may arise because of lower incorporation of SiC particles as well as their inhomogeneity distribution through the coating layer which results in a poor coating formation with inferior mechanical and electrochemical behavior. Many researches have reported production of Zn-SiC composite coating without adding additives to the bath such as nano sized of Zn-SiC composite coating under direct current (Sajjadnejad et al., 2014a), under pulsed current (Sajjadnejad et al., 2014b), using pulsed–reverse current (Farde et al., 2010) and under ultrasonic (Gyawali et al., 2012). Pulse, pulse reverse current and ultrasonic techniques are expensive due to high cost of a pulse rectifier as well as other sophisticated regulated equipment used by these technologies (Chandrasekar and Pushpavanam, 2008) which make them uneconomical for producing the composite coating and restrict their applications in industry.

To overcome these limitations, there is growing interest in use of additives in producing the composite coating due to their low cost, availability, easy to apply and can be used with lower quantities. It has been reported that adding some additives to the bath solution could influence the embedment of inert particles into metal matrix to a great extent. The improvement in incorporation rate of inert particles (SiO_2) into zinc matrix was achieved by using N, N-dimethyldodeecm (NND) additives as reported by Tuaweri and Wilcox (2006). They discovered an increase in number of SiO_2 was in when additive was used and concluded that the properties of Zn-SiO_2 composite coatings were enhanced as well. Hou et al. (2002) investigated the effect of CTBA (Cetyirimethyl Ammonium Bromide) additives on the formation of Ni-SiC composite coatings. They found that the adhesion between the suspended particles and the cathode surface was improved and hence resulted in more of SiC particles embedded into coating layer.

The use of additive in producing of Zn-SiC composite coating has not been investigated in previous researches and therefore needs more attention. This study is focused on the improvement of Zn-SiC composite coating by using some additives to bath solution as well as optimization of the operating parameters during electrodeposition process. These composite coatings are produced for various industrial applications in which desired coating properties are required such as excellent wearing properties, good corrosion resistance and high hardness. The composite coating is then obtained from electrodeposition bath containing zinc salts and dispersed ceramic or metal oxide particles.

1.2 Problem Statement

Electrodeposition of Zn-SiC composite coating is affected by various operating parameters such as stirring speed, SiC concentration and current density. Low incorporation of SiC particles may be caused by hydration forces of SiC particles that hinder deposition of SiC particles (Vathsala and Venkatesha, 2011; Tuaweri and Wilcox, 2006). This is due to the nature of SiC particles which is considered as hydrophilic materials that exhibit low tendency for deposition (Suzuki et al., 1987). In addition the agglomeration of SiC particles in the bath solution as well as hydrogen evolution could cause a significantly reduction in the amount of SiC particles in the zinc matrix (Tuaweri and Wilcox, 2006; Hou et al., 2002; Sulaiman, 2014). Therefore, it is essential to understand the effect of these parameters on the formation of composite coating in order to obtain the best conditions. Once these conditions are determined then further improvement in coating characteristics can be achieved.

The use of additive (cetyltrimethylammonium bromide, CTAB) could increase zeta potential of SiC particles by adsorption of cations on the particles surface which lead to changes in the surface charge of SiC particles to more positive (Ger, 2004). The adhesion force between the SiC particles and the cathode surface is then raised and hence increasing of SiC particles into the deposit layer (Lee et al., 2007). In addition, these additives such as cetyltrimethylammonium bromide (CTAB) and N, N-dimethyldodeecm (NND) could reduce the agglomerated particles in the bath solution and hydrogen evolution which results in acceleration of SiC particles towards the cathode surface and deposited on it (Hou et al., 2002; Ger, 2004; Tuaweri and Wilcox, 2006). The microstructure of the composite coating could be affected by addition of additives to the bath solution in which the microstructure becomes finer and resulting in increase of mechanical and corrosion properties as well (Sharifalhoseinio et al., 2016).

Using niobium in production of other coatings such as nickel composite coating has been reported to improve corrosion properties (Fratari and Robin, 2006; Banczek et al., 2010). Niobium could change the microstructure of nickel coating to fine structure which results in high corrosion resistance. The surface charge of inert particles could become more positive using additives (Lee et al., 2007; Hou et al., 2002). Niobium chloride could change the surface charge of dispersed particles to more positive due to rising in zeta potential value which results in more inert particles attached to the cathode surface and hence increasing incorporation rate. Niobium chloride is used as a source of niobium in the bath solution which could change the microstructure of the coating to fine structure (Rodrigues et al., 2014). Also niobium could accelerate electrodeposition process by reducing hydrogen evolution (Bard, 1974). On the other hand, the presence of phosphoric acid in producing of

Ni-P/ZnO-SiO_2 coating has been found to increase the embedment of SiO_2 into nickel matrix and improving the corrosion behavior of the coating (Sharifalhoseinio et al., 2016). Phosphoric acid could prevent the agglomeration of particles and forming a well dispersed composite coating. Also zeta potential could be raised using phosphoric acid and hence increase positive charges on the surface of inert particles which results in more particles to be attracted to the cathode surface. Phosphoric acid is the main source for phosphorus ions in the bath (Sulaiman, 2014). The microstructure of zinc coating could be affected by presence of phosphoric acid which results in fine and compact structure (Sandu et al., 2012; Weng et al., 1997; Tamilselvi et al., 2015; Dini, 1993; Zhang et al., 2008).

Most of researches were focused on the formation of Zn-SiC composite coatings and studied the morphology of those coatings including the incorporation of SiC particles into zinc matrix. Few investigations were performed on corrosion and mechanical behavior of Zn-SiC composite coatings. Therefore, there is a need for an investigation of corrosion behavior, EIS studies, microhardness property and adhesion of Zn-SiC composite coatings. Using a micron sized of SiC particles for producing of Zn-SiC composite coating has not been investigated by previous researches. Also using additives in producing Zn-SiC composite coating are rarely reported. In addition, no studies have been conducting to study EIS and adhesion of the produced this composite coating. Poor coating adhesion could lead to remove the coating layer and expose of the metal surface to severe environmental conditions. EIS is an important procedure to study corrosion mechanism of the coating in which the coating resistance and charge transfer resistance can be evaluated.

Therefore, this research intended to produce a good Zn-SiC composite coating with significant improvements in corrosion and mechanical properties by addition of niobium chloride and phosphoric acid as additives to the bath solution during electrodeposition process. Few studies have been performed on the effect of additives on the formation and properties of Zn-SiC composite coating. However, suitable amount of niobium chloride and phosphoric acid additives in electrodeposition bath must be defined to produce Zn-SiC composite coatings on mild steel with good corrosion and mechanical properties.

Micron sized SiC particles are easy to co-deposited in comparison with nano sized particles when electrodeposition conducting under direct current. Micron sized SiC particles are cheap and readily available. The mass transport of particles towards the cathode is better when using micron sized particles. A lot of researches try to improve the composite coating using nano SiC but using nano under direct current found to be hard to incorporate within metal matrix, this was due to high agglomeration of nano sized particles in the bath when deposited under direct current. To overcome this problem electrodeposition with nano particles was performed under Pulse and pulse reverse current which induced more cost. Pulse and pulse reverse techniques are expensive due to high cost of a pulse rectifier as well as other sophisticated regulated equipment used by these technologies which make them uneconomical for producing the composite coating and restrict their applications in industry. In addition nano size more expensive than micron size particles.

To overcome these limitations, there is growing interest in use of additives in producing the composite coating due to their low cost, availability, easy to apply and can be used with lower quantities. So the main reason using micron size to get

good coating at low cost and using simple equipment. Deposition of micron SiC with using additives shows good results compared with nano SiC and at low cost. Therefore, this study will rebound the preparing a good composite coating with low cost as well as propose the mechanism how niobium chloride and phosphoric acid improve the coating properties.

1.3 Research Objectives

The main aim of this research is to produce Zn-SiC composite coatings on mild steel and to overcome the problems related to low corrosion and mechanical properties of Zn-SiC composite coatings.

1. To investigate the influence of electrodeposition operating parameters such as stirring speed, SiC concentration and current density on the formation and properties of Zn-SiC composite coating in order to determine the best operating conditions for electrodeposition of Zn-SiC composite coating.
2. To characterize the mechanical properties of Zn-SiC composite coating deposited in the presence of niobium chloride and phosphoric acid additives.
3. To study the effect of niobium chloride and phosphoric acid additives to the bath solution on corrosion behavior of Zn-SiC composite coating.

1.4 Scopes of the Study

Based on limitations in the literature, this study was focused on electrodeposition of Zn-SiC composite coating on mild steel and to improve the properties of Zn-SiC composite coating. Different types of additives namely niobium chloride and phosphoric acid had been studied to tackle the problems of low

incorporation rate of SiC particles into coating layer, Zn-SiC structure as well as low corrosion and mechanical properties of the composite coating. In general, this study was divided into two parts.

The first part is a preliminary study in which electrodeposition process was conducted to deposit of Zn-SiC composite coatings on mild steel surface. In this study, the effect of operating parameters (stirring speed, SiC concentration and current density) on deposition of Zn-SiC composite coating was thoroughly investigated. The composite coating was then characterized using XRD, SEM, corrosion and microhardness behavior.

The second part was focused on enhancement of Zn-SiC composite coating by adding some of additives such as niobium chloride and phosphoric acid to the bath solution and the deposition process was conducted under the best operating conditions obtained from preliminary study. In this part, coating thickness, microhardness, adhesion bond strength, corrosion and impedance behavior of Zn-SiC composite coating were explored in order to understand the effect of the niobium chloride and phosphoric acid additives on the microstructure and properties of Zn-SiC composite coating.

1.5 Thesis Organization

This thesis consists of five chapters, the chapters are outlined as follows:

Chapter One briefly provides an introduction of the research work which includes research background and problem statement. The research objectives and

scope of study were also specified in order to obtain Zn-SiC composite coating with good properties.

Chapter Two covers metal coatings, techniques for conducting of metal coatings, description of electrodeposition process, details on composite coatings, review of operating parameters that affect electrodeposition of Zn-SiC composite coating and finally evaluation of Zn-SiC composite coating was also pointed out.

Chapter Three describes the materials and apparatus used in this research work. Experimental set up and procedure were detailed out. The characteristics techniques used in this study were also explained.

Chapter Four presents results and discussion on Zn-SiC composite coating formed on mild steel. Two parts were presented in this chapter. The first part covers the preliminary study which is about the influence of operating parameters on the deposition of Zn-SiC composite coating in order to get the best parameters that could lead to produce a good Zn-SiC composite coating. The second part presents the deposition of Zn-SiC composite coating under the best operating conditions obtained from preliminary study and in presence of niobium chloride and phosphoric acid additives.

Chapter Five provides a conclusion of major findings of this study and gives recommendations for future works in this field.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

In this chapter, metallic coatings especially zinc coatings on steel substrate are reviewed including the technologies used for deposition of zinc coatings on steel substrate. Electrodeposition process is described in details with a highlight on the deposition mechanism for formation of composite coating. The studies that conducted on the formation and properties of various zinc composite coatings are reviewed and reported. The effect of operating parameters on the composition and properties of these coatings are addressed. The problems that generate from incorporation of SiC particles into zinc matrix are presented and the solutions to overcome these drawbacks are indicated. Finally, the corrosion behavior, electrochemical impedance spectroscopy (EIS) studies, microhardness measurements and adhesion property that used to evaluate the composite coating are reviewed.

2.2 Metallic Coating

Protective coating on steel structures is one of major corrosion control approaches. It is used for long term protection of steel components under various corrosive conditions (Fayomi et al., 2016). A satisfactory barrier between steel surface and the environment can be provided by a thin layer of metallic coating (Fontana, 1987). Selection of the coating will be depended on the desirable property that required for specific application. For example, antifouling coating is used for inhibition of the growth of organism on the coating. With regards to corrosion prevention, the main function of the coating is to provide a corrosion resistance in corrosive environments

(Roberge, 2000). The protective coatings can be classified into organic, inorganic and metallic coatings. Metallic coatings are preferred in corrosion protection since exhibit some of formability in comparison with inorganic coatings which are more brittle (Fontana, 1987). Metallic coatings could change the substrate properties of steel structures. The corrosion resistance can be provided by metallic coatings whereas the steel substrate offers a load bearing capability.

From corrosion point of view, metallic coatings can be classified into noble and sacrificial coatings (Chatterjee et al., 2001). The direction of the current flow for both noble and sacrificial coatings is presented in Figure 2.1. Noble coatings used metals that are nobler than steel in galvanic series such as nickel, copper and chromium. It has been reported that the presence of pores on this type of coatings could accelerate the corrosion of the base metal. This is due to the direction of galvanic current at the pores which leads to rapid attack of the metal surface and underneath the coatings (Schweitzer, 2004). Therefore, noble coatings should be produced with low number of pores in order to prevent the access of the water underneath the base metal. In sacrificial coatings, the direction of galvanic current is from the coating to the surface of the base metal. This leads to cathodically protection of the base metal (i.e. the base metal will not be corroded as long as the current flows and there is electrical contact with the coating) (Uhlig and Revie, 1985; Igcse, 2019). The most important sacrificial coatings are cadmium, zinc and alumium.

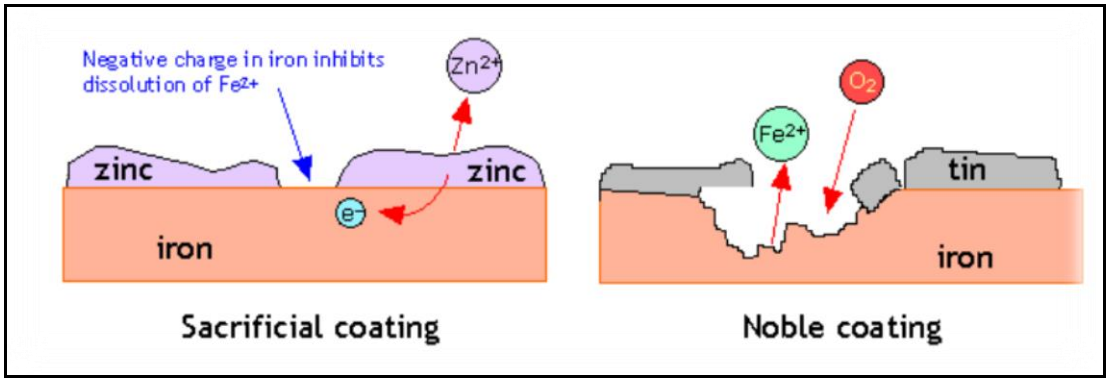

Figure 2.1: Noble and sacrificial coatings (Igcse, 2019)

2.3 Zinc Coating

Zinc is one of major coating metals used in industrial sector. It is used as a protective coating for numerous of metal products and fabricated parts (Popoola et al., 2016). A large quantity of zinc is consumed where corrosion resistance is a major concern (Tuaweri, 2005). It has been reported that 25% of the production of zinc used for producing zinc alloys coatings in USA (Seah, 1996). Zinc coatings exhibit better corrosion resistant to both atmospheric and marine environments. It has been found that zinc coating with thickness of 0.03 mm lasts 11 and 8 years in rural atmospheric and marine environments respectively (Uhlig and Revie, 1985). Zinc coating is preferred for protecting of steel and iron. Zinc is anodic to steel which could offer a cathodic protection to the steel. The galvanic series exhibited zinc is more active than steel and hence sacrificed to protect the steel surface. Zinc coating acts as a sacrificial anode and protects underneath steel surface from the corrosion (Sancakoglu et al., 2011).

However, zinc coating should be free from defects, compact and dense to prevent corrosive environment attacks (Hu et al., 2018). In order to produce a good

zinc coating, various techniques are used to apply zinc coating on steel substrate. Figure 2.2 shows the methods used for the deposition of zinc coatings.

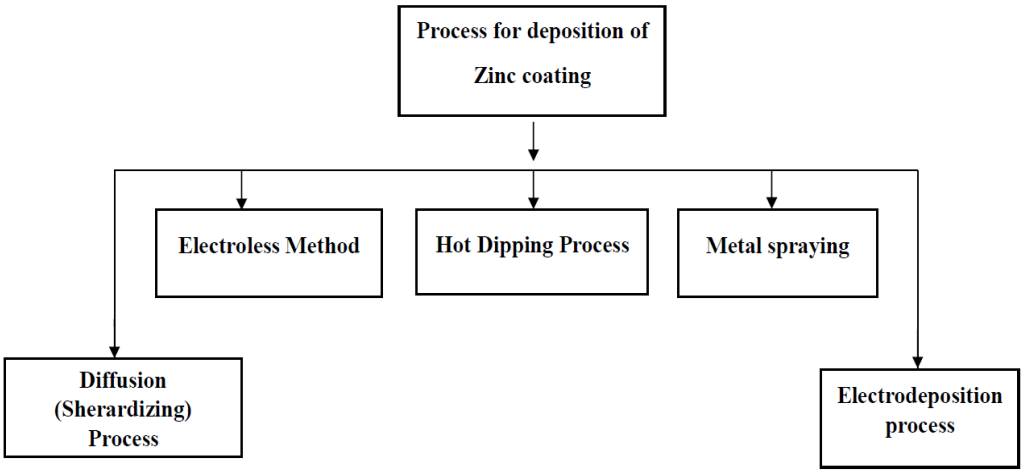

Figure 2.2: Processes used for deposition of zinc coating (Porter, 1991)

The major methods used for deposition of zinc coating are summarized as follows (Uhlig and Revie, 1985):

2.3.1 Hot Dipping Process

Hot dipping is a process for conducting zinc coating on the steel structure. In this process the steel parts are immersed in a molten zinc bath (Fontana, 1987). Many components in automotive industry are coated by this method (Roberge, 2000). The main drawbacks of this method are its difficulty in producing thin thickness, it can be applied only in galvanized plant not at the site as well as limited structure size.

2.3.2 Metal Spraying

In this process, a metal wire or powder is feeding through a melting flame. The molten metal is then blown on the steel surface by using high velocity stream or

compressed gas. The bonding between the coating and steel surface obtained by mechanical bonding with a roughened substrate or localized diffusion (Roberge, 2000). Using expensive apparatus and low coating quality are limited the use of this process.

2.3.3 Electroless Method

Electroless is defined as chemical reduction process (Roberge, 2000). No electrical energy used in this process. It depends on the catalytic reduction of the metal ions in the solution. In this process, reduction of metal ions takes place on the catalytic surface. When the metal is immersed in the solution bath, the metal ions in the solution can be discharged by chemical reductant R^{H+} in the solution (Kanani, 2004). Although this process offers uniform thickness but has some disadvantages. These include depleted of metal ions from the solution not from anodes and the solution should be heated to 190 Fº.

2.3.4 Diffusion (Sherardizing) Process

The sherardizing process involves diffusing of the zinc into the base metal of the object to form the coating. This can be done by packing the steel pieces in solid material or by using gaseous that containing the metal coating (Fontana, 1987). It can be applied on small pieces only and the control of this process is difficult.

2.3.5 Electrodeposition

Electrodeposition process is considered as a surface finishing technique that used to enhance the surface properties of the metals such as corrosion, wearing and hardness (Sancakoglu et al., 2013). A uniform, dense and adherent coating can be produced by electrodeposition process (Lou and Huang, 2006). In electrodeposition

process, a current is passed through the deposition bath and between the anode (metal to be deposited) and the cathode (workpiece to be plated) (Lou and Huang, 2006; Kanani, 2004). During electrodeposition process the dissolution of the anode takes place while the cathode surface covered with the deposit metal. Electrodeposition technology is widely used for coated various industrial components. Figure 2.3 presents the stages of electrodeposition process that used in industry.

Among those technologies, electrodeposition process is the most promised technology that used for producing of zinc coatings on steel surface. It has many advantages compared with other technologies. Electrodeposition is a cost effective method, a smooth surface coating can be produced by this process, it provides a better coating bonding, coating thickness can be easily controlled, it might be used for deposition of metallic alloys as well as composite coatings (Sancakoglu et al., 2011; Ciubotariu et al., 2008; Badarulzaman et al., 2009). It used to deposit nanostructured layers on materials surface and can be applied on irregular and complex shapes (Ullal and Hegde, 2013). It discharges fewer wastes and hence reduces a contamination level compared with spraying and hot dipping technologies. Low energy required (Saha and khan, 2010; Mohler, 1969). Electrodeposition process exhibits high production rates and can be operated continuously (Tuaweri and Wilcox, 2006; Jean et al., 1999; Lowenhetim, 1974).

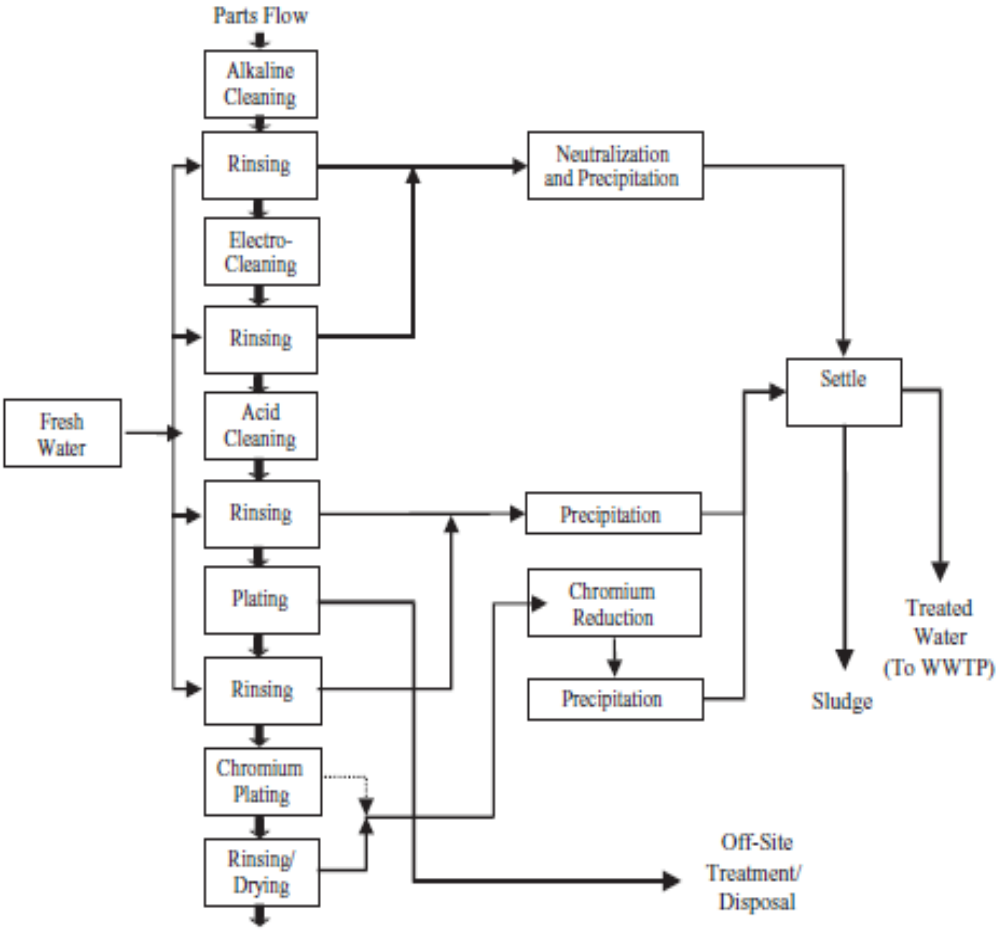

Figure 2.3: Electrodeposition stages (Lou and Huang, 2006)

The produced electrodeposited zinc coating without subsequent treatment leads to change in the appearance of the coating to dull grey when exposed to air (Fayomi et al., 2015; Xu et al., 2008). In addition, these coatings are subject to corrosion to small extent (Praveen and Venkatesha, 2008). The formation of white rust corrosion on zinc coating would affect and reduce the service life of zinc coating (Vathsala and Venkatesha, 2011).

2.4 White Rust Corrosion

White rust corrosion is a natural corrosion process that occurs on fresh zinc coated structures. It is considered as corrosion product of zinc and can be formed when

zinc coating exposed to specific operational conditions (Orrcon, 2005). White rust corrosion has a white waxy deposit which can be clearly observed as shown in Figure 2.4. This deposit might be zinc oxide or zinc carbonate or zinc hydroxide (Tata, 2013). The mechanism for formation of white rust corrosion will be depended on many factors. Water chemistry is the main variable that affects forming of white rust corrosion. Since the mechanism of white rust corrosion vary from system to system it is important to understand the conditions that could cause this type of corrosion.

White rust corrosion might be zinc oxide $3Zn(OH)_2 . ZnO_2 . H_2O$ (Awt, 2012). This oxide is characterized with porous structure and hence will be unable to protect the zinc surface from the exposure to the environment (i.e. protect zinc surface against oxygen in water) (Porter, 1991). Therefore, the corrosion continues as long as there is moisture on the zinc coating surface. Zinc protective film would be depleted and general corrosion initiated on the metal surface in case of removal or disrupt of zinc oxide layer.

Figure 2.4: White rust corrosion formed on zinc coating (Orrcon, 2005)

Another form of white rust corrosion is zinc carbonate that produced the compounds of $ZnCO_3$. $3Zn(OH)$. H_2O. Figure 2.5 illustrates the white rust corrosion mechanism. The formation of this type of corrosion can be explained as, water contains several of contaminants which include dissolved chemical compounds and gases as well as suspended particles (Kem, 2014). The concentration of these contaminants increases with the time in which water losses by evaporation. This might lead to increase in the alkalinity of carbonate and pH as well. This accelerates the corrosion process of zinc layer. Therefore, white rust corrosion needs more attention as it might cause damage to the protective zinc layer. The corrosion could be continued until reach the base steel surface. In addition, localized corrosion cells on steel surface (underneath zinc layer) might be induced by white rust corrosion (Kem, 2014). This could lead to ferrous metal corrosion (red rust corrosion) and eventually the failure of the component might be caused.

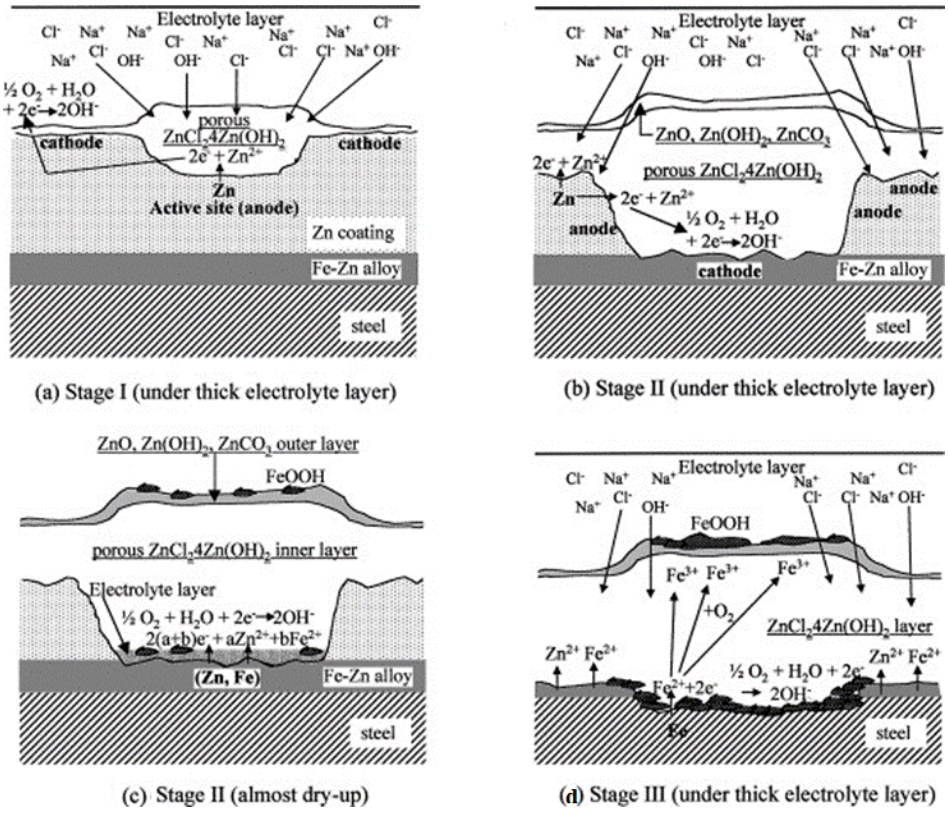

Figure 2.5: White rust corrosion mechanism (Yadav et al., 2004)

In order to prevent white rust corrosion, zinc coatings are subjected to post deposition treatment such as chromate conversion process (Hu et al., 2018). The chromate solutions used for post deposition treatment are Chromic acid (Cr(VI)) solution (Ranganatha et al., 2012; Maeda and Yamamoto, 1998) or a mixture solution of trivalent and hexavalent chromate (Lin et al., 2008; Xu et al., 2008; Yu-ye et al., 2007). The chromate conversion process results in the passivation of zinc coating surfaces. Recently, chromate treatment process for zinc coating is avoided due to environmental concerns which are summarized as:

(1) The effluent discharged from chromate process is hazardous and could impact the environment (Ranganatha et al., 2012; Praveen and Venkatesha, 2007) which might lead to water and soil contamination;

(2) Chromium used in chromate process is considered as a heavy metal that has carcinogenic nature in which a serious hazard to human life could be caused (Hu et al., 2018) and (3)

The chromate process is toxic and when exposed to atmosphere, an oxide layer is formed which is permeable to further oxygen contamination (Praveen and Venkatesha, 2008).

All these problems have promoted the extensive investigation in this area and suggestions for the replacement of this chromate process have been adopted. The available alternative strategy is to enhance the properties of the coating surface rather than post deposition treatment process (Vathsala and Venkatesha, 2011). In this regard, the researches have been focused on the developments of zinc based alloys coating. An example of zinc based alloy coatings are Zinc–Aluminum, Zinc–Nickel alloy and Zinc-Tin alloy coatings (Panossian et al., 2005; Manna, 2011). However,

determination percentage of alloying elements is critical which could affect the properties of zinc coating (Ramanauskas et al., 1997). Alternative approache is zinc composite coating. The main idea for development of composite coating is to combine the best properties of different materials in order to get one materials with supper properties. The excellent corrosion protection property of zinc and the high mechanical properties of SiC, Al_2O_3 and WC can be combined using electrodeposition process to produce zinc composite coatings (Sancakoğlu, 2009).

2.5 History of Composite Coating

In general, composite materials are fabricated from two phases and more. The properties of composite materials are superior to independent phase. The main phase in composite is named as matrix whereas the reinforcement is referred to the second phase. Various materials are used as reinforcement in the composite. This includes fiber, polymer, ceramics, metal oxides and carbides, sandwich materials and dispersion – strengthened alloys (Tuaweri, 2005). Composite coatings are produced by electrodeposition process using bath solution containing metal salts and inert suspended particles. The composite coating is then produced from the reduction of metal salts ions that forms a thin layer of the metal and inert particles.

Composite coating produced by electrodeposition process was first patented in 1950s in which graphite-copper composite coating was produced. The developments of composite coating were continued progressively in 1960s and researchers were focused on producing of Ni-SiC composite coating to be used for friction parts. Researches about corrosion, tribiological and mechanical properties of nickel composite coatings started in the period of 1970s (Low et al., 2006). During

1990s, the physical properties of the composite coatings were investigated (Musiani, 2000). In this decade, nano particles and electro catalysts are introduced in producing of composite coatings. In recent years, the development of zinc composite coatings has been shown a high research interest. In this technology, zinc metal is electrodeposited with polymers, ceramics and metal oxides particles on steel substrate. Bath solution containing soluble zinc salts and dispersed particles are used to obtain the composite coating (Hovestad et al., 1995).

2.6 Zinc Composite Coatings

Zinc coating is widely used in industrial sector due to its low cost and good corrosion resistant to both atmospheric and marine environments. It is used as a protective coating for numerous of steel products (Popoola et al., 2016). Zinc coating provide a sacrificial cathodic protection to the steel which is considered as effective and economic approaches for protecting of steel structures.

Increasing demand of industrial applications requires improvement of zinc coating. In order to enhance zinc coating properties, a new technology is developed. This includes generation of zinc composite coating on steel surface by electrodeposition process. The produced composite coatings exhibit better properties than ordinary zinc coatings. Recently zinc composite coatings have been studied and their properties have been improved. This includes a good wearing and corrosion resistance, high temperature inertness, dispersion hardening, self-lubricity (Sajjadnejada et al., 2014b; Sancakoglu et al., 2011), better tribiological properties (Praveen and Venkatesha, 2008; Roventi et al., 2017), good hardness (Popoola et al., 2016), better strength behavior and high stiffness property (Fayomi et al., 2016).

Zinc composite coatings are produced by dispersing of hard particles such as ceramics, metal oxides and metal carbides in zinc salts solution (Praveen and Venkatesha, 2008). Various types of composite materials are used in producing zinc composite coatings such as TiO_2, SiO_2, ZrO_2, CNT, WC, Al_2O_3 and SiC (Fayomi et al., 2016). Embedment of these hard particles into zinc matrix shows significant enhancement in mechanical and corrosion resistance properties (Burzynska et al., 2008).

Incorporation of ZrO_2 into zinc matrix has been found to improve corrosion resistance of the composite coating (Vathsala and Venkatesha, 2011). Fayomi et al. (2016) prepared Zn-Al_2O_3-SiC composite coating with increasing in corrosion resistance of the coating. The presence of TiO_2 in zinc coating has been studied by Praveen and Venkatesha (2008) and they concluded that TiO_2 led to enhancement in corrosion behavior of the composite coating compared with pure zinc coating. Zn-SiO_2 composite coating was produced by Tuaweri and Wilcox (2006) and they reported that SiO_2 particles have a positive effect on the coating properties. Ranganatha et al. (2012) reported that Zn-CeO_2 composite coating formed by electrodeposition process exhibited better corrosion and mechanical properties. Zn-Al_2O_3 was successfully deposited on the brass surface using electrodeposition technique by Sancakoglu et al. (2011). They obtained a homogenous composite coatings with better properties. According to Popoola et al. (2016 b) the deposition of Zn-ZnO-Y_2O_3 on mild steel has increased the hardness and corrosion resistance of steel substrate.

Although several studies were conducted on zinc composite coatings, a few researches have been reported on producing of Zn-SiC composite coatings. These researches were focused on study the morphology of the composite coating. The